COLE

The Sorption of Hydrogen Bromide by

means of Anhydrous Copper Sulphate

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THE SORPTION OF HYDROGEN BROMIDE BY MEANS OF ANHYDROUS COPPER SULPHATE

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED The Sorption of Hydrogen Bromide by Means of

Anhydrous Copper Sulphate

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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INTRODUCTION.

Chapter I.

Introduction.

(a) General Theory of Absorption.

It is a familiar fact that when water containing a colour-
ing matter such as caramel or litmus is shaken up with finely
divided charcoal, the latter on settling carries down with it
the colouring matter ,leaving the water practically colorless.
Further investigations show the other substances, including
electrolytes and non-electrolytes as well as colloids, are
largely taken up by charcoal from aqueous solution, and that
other finely divided substances have the same property. Char-
coal has also the power of taking up great quantities of gases,
especially those which are easily liquified, such as ammonia
and sulphur dioxide.

(b) Acetic-acid and Charcoal.

The nature of this phenomenon will be more readily under-
stood in the light of some quantitative observations. For this
purpose the results of a series of experiments carried out by
Schmidt (1) on the taking up of acetic acid from aqueous so-
lution by charcoal are quoted. Animal charcoal in quantities
of five grams was taken up with aqueous solutions of acetic
acid (100 c.c. in each case) of different concentrations, and
the amount of acid remaining in the water phase determined by
titration. In the accompanying table, Ac represents the amount
of acetic acid taken up by the charcoal, and Aw the amount left
in solution at equilibrium.

Distribution of Acetic Acid between Water and Charcoal.

Ac	0.93	1.15	1.248	1.43	1.62
Aw	0.0365	0.084	0.13	50.206	0.350
C_{c}/Cw	205.	208.	180.	203.	197.

As the volume of the solution and the amount of charcoal are
kept constant,the amounts given in the table are proportional
to the respe(c)tive concentrations, Cc and Cw,in the two phases.
The figures show (1) that in very dilute solution the acid
is almost completely taken up by charcoal; (2) that the con-
centration in the charcoal increases much less rapidly than the
concentration in the aqueous phase. That we are dealing with
true equilibra is shown by the fact that the same results are
obtained from either side (starting from the concentrated or
from the dilute solutions of the acid).

The question now arises as to how these observations are to
be interpreted. In the first instance we will consider whether
the process is a physical or a chemical one,and if the former,
whether it is mainly a surface condensation or whether solid
solutions are formed.

It appears highly improbable for several reasons that the
phenomena are chemical in nature. In the first place,the most
widely different substances,including argon and other inactive
gases,which do not as far as is known enter into chemical com-
bination,are taken up by charcoal. Further, a definite chemi-
cal compound is constant in composition,and,if undissociated,
its composition is independent of the concentration in the
other phases,whereas,as the table shows, a composition of the

carbon-acetic acid system varies continously within wide limits.
At first sight it would appear possible to explain the results
as being due to the formation of a partially dissociated solid
compound in equilibrium with its products of dissociation, but
it can easily be shown that the assumption also is incompati-
ble with the facts. Applying the law of mass action to such
an equilibrium (in the liquid phase), we have,-

$$(\text{Absorbant})^{n_1} \ (\text{Substance taken up})^{n_2} / (\text{Compound})^{n_3} = \text{Constant}.$$

The active mass of a solid substance at a definite temperature
is constant, i.e., independent of the amount of solid present.
The parentheses represent concentrations, and n_1, n_2, and n_3
represent the number of molecules of the absorbant (charcoal),
the substance taken up (acetic acid), and the compound respec-
tively taking part in the equilibrium. Further, since the
active masses of the charcoal and the compound are constant

$$(\text{Substance taken up}) = \text{Constant (in liquid phase)}$$

that is, the concentration of the acetic acid in the solution
must be constant as long as both solid phases are present. As
a matter of fact, the concentrations of the acetic acid in the
solution increases continuously with the total concentration
(compare table), so that no second solid phase (no chemical com-
pound) can be present.

The formation of a solid dissociating compound from a solid
phase and a substance in solution has been investigated by
Walker and Appleyard (2) in the case of diphenylamine and pic-
ric acid, which combine to form the slightly soluble brown com-
pound diphenylamine picrate. Until the concentration of the

acid in the aqueous layer reached 0.06 moles per litre, the
solid diphenylamine (which is practically insoluble in water)
remained colorless. On further addition of picric acid, the
brown diphenylamine picrate began to form, and, finally, prac-
tically all the diphenylamine was converted into picrate, the
concentration of the picric acid in the solution remaining all
the time practically constant at .06 moles per litre. It is
evident from this that the system exactly corresponds to the
well known calcium carbonate-calcium oxide- carbon dioxide
equilibrium except that in the latter case the substance of
variable concentration (the carbon dioxide) is the gaseous and
not in the liquid phase.

It remains to consider whether the phenomena in question,
such as the taking up of acetic acid by charcoal, are due to
surface condensation or whether solid solutions are formed.
It would seem probable to decide this question at once by ob-
serving the rate of establishment of equilibrium, since surface
condensation must be a very rapid process, and the formation
of a solid solution, whereby(in the case under consideration)
one substance has to diffuse into the interior of the other,
must be a relatively slow process. As a matter of fact the
establishment of equilibria in many cases (but not in all cases,
see below) is usually quite rapid, which lends strong support
to the surface condensation theory. The most decisive char-
acteristic distinguishing between the two phenomena, however,
is brought out by a consideration of the ratio of the distri-
bution of the substances between the two phases. It has been
shown that when a substance distributes itself between two

phases the ratio of the distribution is independent of the molecular concentration, provided the molecular weight of the solute is the same in both solvents, but if the molecular weight in the solvent (A) is (n) times that in the solvent (B), then $\sqrt[n]{Ca/Cb}$ is a constant, which may be written more conveniently thus :- $C_A^{1/n}/C_B =$ Constant. Now the table given above shows that for the distribution of acetic acid between water and charcoal the formula holds approximately $C_C^4/C_W =$ Constant, where C_C and C_W represent the concentrations in charcoal and in water respectively. Comparing this with the distribution formula $C_A^{1/n}/C_B =$ Constant, we find that $1/n=4$ or $x=\frac{1}{4}$; that is, if charcoal and water may be regarded as two solvents between which the acetic acid is distributed, then the molecular weight of the acid in charcoal is $\frac{1}{4}$ that in water. Now it was shown by Raoult that acetic acid exists as single molecules in aqueous solution, so that its molecular weight in charcoal, deduced on the assumption that it is present in solid solution, is an impossible one . Analogous results are obtained with other solutes and other absorbing agents, and it follows at once that the "solid solution" explanation of the phenomena under consideration is definitely disproved for certain cases. There is evidence, however, that in some cases solid solution may play a subsidiary part in the phenomena. Thus Davis (3) found that when iodine is shaken with charcoal a very rapid action is followed by a slow action, the latter being presumably due to slow diffusion of the iodine into the interior of the charcoal. Similarly McBain (4) has shown that when hydro-

gen which has been in contact with charcoal for a long time
is pumped out,the greater part of it (that condensed on the
surface) can be drawn off immediately,but a small residue
(presumably present in solid solution) can only be removed
very slowly.

It has now been established that the phenomenon called ab-
sorption is physical in nature and mainly at least due to sur-
face condensation...In order to distinguish it from such a
process as the absorption of gases in liquids,an example of
true solution,the process is termed adsorption,and the sub-
stance which is condensed on the surface of the solid phase is
said to be adsorbed.

(c) Adsorption of Gases.

Thus far only adsorption of substance from solution has been
considered,but it has long been known that porous substances
have a considerable adsorptive power for gases,and that those
gases which are most easily liquified are most largely adsorbed.
The nature of the results is well shown by the recent accurate
work of Homfray (5) and Titoff (6) on the adsorption of gases
by charcoal. The amount of gas adsorbed is found to be pro-
portional to the adsorbing surface and the greater the lower
the temperature and the higher the pressure. Titoff found
that the adsorption formula of hydrogen follows Henry's Law ,
so that the formula

$$C_A \Big/ C_B = \text{Constant},$$

applies where C_A represents the concentration in the solid
phase, C_B , that in the gas phase. The other gases at low tem-
peratures do not follow Henry's Law,but the results are repre-

sented fairly satisfactorily by a formula of the type

$$C_A^{1/n} \Big/ C_B = \text{Constant}.$$

It has been shown above that a formula of the type

$$C_A^{1/n} \Big/ C_B = \text{Constant}$$ -an exponential formula - affords a fairly satisfactory representation of the adsorption both of gases and dissolved substances. In the literature it is often met with in a slightly different form in which instead of writing $C_A^{1/n} \Big/ C_B$ can be written $C_A \Big/ C_B^{n} = C_{ow}$. When for C_A, n/m. is placed where (n) represents the amount of substance adsorbed by (m) grams of adsorbent, we obtain, putting p for C_B and $1/n$ for (n), the formula $\frac{n}{m} = \beta \, p^{1/n}$ where β and n are constant at constant temperature. When $1/n = 1$ the adsorption follows Henry's Law, but in almost every instance $1/n$ is considerably less than 1 . This expresses the important fact that adsorption is relatively greatest from dilute solutions and falls off rapidly with the concentration.

(d) The Cause of Adsorption.

Adsorption of gases and liquids occurs more or less at all solid surfaces, a well known case in point being the adsorption of moisture by glass surfaces, but it is only when the surface is very large in comparison with the weight of the solid - as in the case of porous and finely divided substances- that it can be readily measured. It is now necessary to consider why the concentration in the surface layers differs in so many cases so greatly from that in the main bulk of the liquid or gas phase. It seems probable at the outset that
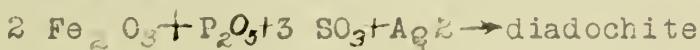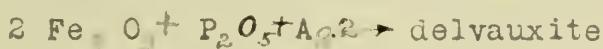
this must be connected with molecular attraction at the boundary of the phases, in other words with the surface tension, and the connection between surface tension and adsorption has been deduced theoretically by J.J.Thomson. From the general standpoint it is necessary to assume that not only increased concentration, but in certain systems of lowering of concentration at the surface, as compared with that in the main bulk of liquid, may occur. Calling an increase of concentration positive adsorption and a dimunition negative adsorption, the rule may be expressed as follows (7). A dissolved substance is positively adsorbed when it lowers the surface tension, negatively adsorbed when it raises the surface tension. The first case is met with in most solutions of organic compounds, the second in solutions of highly ionized inorganic salts.

(e) Adsorption of Gases By Substances Containing
Combined Water.

In the light of the work done along these lines, the question has arisen as to whether many of the adsorption and addition phenomena which are usually attributed to chemical interaction are not in some way closely connected to adsorption. Specific instances have been worked out by various investigators, which have resulted in the conclusion that the adsorption phenomenon is a much more common occurence than chemical interaction. (8) By adsorption, hydrogels may take up and hold acids, alkalis, salts, etc., dissolved in water, in such quantities that sometimes the resulting products may be mistaken for chemical compounds. Following the investigations of van Bemmelen, Bilitz

and Behre (9) have shown recently that the compound of arsenic
acid with ferric oxide ,which Bunsen considered basic ferric
arsenite, $4Fe_2O_3$, As_2O_3, $5H_2O$ is as a matter of fact an
adsorption compound in van Bemmelen's sense. By adsorption
there arise complex bodies from the simple -(10) e.g. the fol-
lowing series :-

$$2\ Fe_2O_3 + 3\ H_2O \xrightarrow{p} Stilnosiderite$$

$$2\ Fe_2O_3 + P_2O_5 + Aq2 \rightarrow delvauxite$$

$$2\ Fe_2O_3 + P_2O_5 + 3\ SO_3 + Aq2 \rightarrow diadochite$$

(11) It was found that in removing water from colloidal hy-
droxides,different chemical compounds holding varying amounts
of water are not formed by stages,but the water content of these
hydrates changes continously. They give up the requisite
amount of water in order to equalize the vapor pressure of the
gel with its surroundings.

Of considerable interest in this connection is the work
done by Kane (12) on treatment of anhydrous copper sulphate
with dry hydrogen chloride. It was found that when copper sul-
phate either quite dry or in the finely powered condition,
retaining one molecule of water,was placed in an absorption
tube and dry hydrogen chloride passed over it ,a rapid absorp-
tion of gas occured with the production of great heat and also
a certain amount of green crystals and a chocolate-brown ma-
terial possesing very interesting properties as described be-
low. After cooling and weighing,the absorption bulb was found
to have taken up somewhat more than one molecule of hydrogen
chloride,the excess being attributedto the quantity absorbed

by the disengaged water. The absorptions seldom obtained the
theoretical amount of one molecule exactly but always approx-
imated it .

When the above mentioned chocolate colored substance was
heated,it readily parted with its hydrogen chloride,leaving
behind the sulphate of copper unaltered. Exposed to the air
it readily absorbed water,with evolution of heat,and assuming
an apple-green color,a change which occured instantaneously
if a few drops of water were allowed to fall upon it. From its
aqueous solution sulphuric acid and crystals of cupric chloride
were obtained. Kane advances two theories which may account
for the properties of the body formed: one,that the chloride
of hydrogen is absorbed by the copper sulphate and combined
with it in the same manner that water would be,-that in fact the
hydrogen chloride is capable of replacing the water of crys-
tallization of salts as ammonia,phosphuretted hydrogen have
been shown to do by Rose and Graham ; the other, that the
chloride of hydrogen reacting on the oxide of copper, forms
water and chloride of copper, while the latter with the sul-
phuric acid constitutes a sulphate of a chloride. An experi-
ment of a similar nature was carried by Colson (13) who used
lead sulphate and hydrogen chloride,but his results seemed to
point mainly in the direction of a double decomposition re-
action.

Still other investigations carried by Von Paul Rohland (14)
seem to indicate that the taking up of hydrogen chloride by
the hydrates of aluminum, iron, or silicon, and by such colored
salts as ferric chloride , potassium dichromate,and copper sul-

phate, is mainly due to absorption.

In addition to these, differences of opinion are found in
many other cases,e.g.,Roscoe and Shorlemmer [15] claim that when
either the anhydrous or hydrated copper sulphate are treated
with dry hydrogen chloride a double decomposition ensues with
the absorption of two molecules of hydrogen chloride and the
evolution of heat. Hempel (16) states that hydrogen chloride
dissolves very easily in water, ice, and in salts containing
water of crystallization,as sodium sulphate, copper sulphate,
magnesium sulphate, sodium tetraborate,etc..

Opinions of a similar nature are given by Blair,Neuth (17),
Richards (18), and Gmelin Kraut (19).

EXPERIMENTAL.

Chapter II.

Experimental.

1. Preliminary Run.

(a) Brief Description of Run .

The object of the work done in this experiment was to determine the exact nature of the reactionor reactions involved in the process of taking up hydrogen bromide by anhydrous copper sulphate.

The first experimental work done in this connection consisted of a preliminary run in which an attempt was made to get approximate data concerning the practical working of the reaction. The materials used in this instance were as pure as could be obtained commercially and consisted of copper sulphate, bromine, red-phosphorus, and calcium chloride. The red-phosphorus was moistened and placed in a litre distilling flask in hte bottom of which a sufficient amount of glass beads were placed to reduce the vigor of the interaction. Inserted in the distilling flask was a 200 c.c. dropping funnel containing the bromine. The delivery tube of the distilling flask entered a simple purifying train consisting of a U-tube containing glass beads mixed with moistened red-phosphorus, and a straight tube containing calcium chloride to serve as a drying agent. This train connected directly to two glass-stoppered weighed U-tubes immersed in cold water,and containing glass-wool, and copper sulphate which had been previously dehydrated. Rubber connections were used in this apparatus.

Bromine was admitted from the dropping funnel a little at

a time to the mixture, uniting with the phosphorus to form
phosphorus-tribromide, the latter of which in the presence of
water was hydrolyzed to hydrobromic acid and phosphorous acid.
The phosphorous acid , being non-volatile,remained in the flask,
while the hydrogen bromide passed thru the train and thence
thru the weighed U-tubes, the contents of which were instantly
blackened upon the entrance of the gas. After passing the gas
for one hour in order to insure a complete interaction, the
tubes were detached and weighed. During the entire passage of
the gas, fumes of sulphur dioxide, organic sulphur compounds,
and unknown substances could be detected in the excess of hy-
drogen bromide being evolved. Although the reaction may have
gone mainly either in the direction of a physical absorption
or a simple chemical addition reaction, the above-mentioned
substances unaccounted for by these and only by complex double
decomposition reactions, were partially formed. The exact
cause to attribute the production of these substances to was
unknown, and, in order to prevent catalytic phenomena from aris-
ing as a result of contact with rubber connections or from the
presence of traces of impurities in the raw materials, pure
reagents and apparatus with all glass connections were used in
all later determinations.

2. Final Run.

(a) Description of Apparatus.

The apparatus consists of a dropping funnel, distilling
flask, drying train, manometer, absorption tube, thermostat.
and a stirring device, and was arranged as follows. The dis-

tilling flask , which was directly attached to the dropping
funnel by means of a ground joint, connected directly to the
purifying train by means of smooth glass joint sealed with
Khotinsky cement. The first piece in the train consisted of
a sealed U-tube containing glass wool, and moistened red-
phosphorus. Next in order came a small preliminary calcium
bromide drying tube, then the large bromide drying tube (D),
and lastly, the tube (C),containing the anhydrous copper sul-
phateand attached to the train by a smooth glass jointclosed
with Khotinsky cement. About midway between bulbs (C) and (A)
and connected to tube (K),which joined the latter bulbs, were
joined two glass tubes running at right angles to each and at
right angles to the tube (K). One of the tubes (E), which con-
tained a stop-cock, led to the water pump,the other tube,(B),
led to the manometer, the latter being so constructed as to
permit the measurement of pressures ranging from zero to two
atmospheres. The absorption bulb (A) was held in the thermo-
stat and maintained at O C. by keeping the two phases,ice and
water in equilibrium with each other. The stirring device con-
sisted of a propeller-paddle driven by means of a water wheel.

(b) Purification and Preparation of Materials.

The purification of the copper sulphate was carried out as
follows. About 800 grams of chemically pure copper sulphate
was dissolved in distilled water, treated with 5 grams of
pure sodium hydroxide, and evaporated until the salt began to
crystallize out. After cooling, the mother liquor was drained

off and the crystals washed with distilled water. The crys-
tals were redissolved in distilled water and the resulting
solution decanted from the precipitate. This process was re-
peated three times in order to remove the impurities com-
pletely. The crystals thus formed were then redissolved in
distilled water, treated with sufficient pure sulphuric acid
to give distinct acidity and evaporated to crystallization.
The mother liquor was decanted off, the crystals washed with
cold water as before , and after redissolving in water and
treatment with a second portion of acid , were again evapor-
ated . This process was also repeated three times. The last
evaporation of this acid solution was so conducted as to ob-
tain crystals about the size of coffee beans, the size being
determined by the concentration of the solution at the point
of crystalization. These crystals were carefully dried and
partially dehydrated on an electric hot plate. It was only
after repeated trials that this substance could be prevented
from crumbling and the initial size and shape of the crystals
maintained until even a partial stage of dehydration had been
reached. When the crystals became white in the dehydration
process,they were removed from the hot plate, placed in an elec-
tric resistance oven, and maintained at a temperature of 500 C.
for twenty-four hours in order to drive off the last molecule
of water, the so-called "Water of Constitution". Altho the
belief that a fractional part of the last molecule of water
of crystallization persists in union with the copper sulphate
at a temperature of 600 C., it was found impossible to go

much above 500° without decomposition ensuing.

One portion of the substance was placed in the absorption
bulb (A), another portion in tube (C) during the process of
constructing the apparatus, and the remainder placed, while
still hot, in a stoppered bottle tightly closed. The tube (C)
which
into the other portion of copper sulphate was introduced was
directly attached to a similar tube containing dry calcium
bromide, the latter having first been fused in a platinum
dish, and then introduced into the tube (D). The copper sul-
phate and calcium bromide were separated from each other by
a narrow-necked tube and sufficient glass wool to prevent the
sulphate from blowing. The entire straight tube was then
placed in a combustion train and gradually heated while a
steady stream of dry air was allowed to pass thru it. This
was continued until a temperature of 400 C. had been maintain-
ed for three hours, at the end of which time the end tips
were sealed with a flame, and the tube connected with the re-
mainder of the apparatus. Calcium bromide was used in prefer-
ence to calcium chloride because it not only avoided the con-
tamination of all the reagents by traces of chlorine which
because
were apt to cause trouble, but also of the greater efficiency
of the bromide for drying purposes. During the purification of
these substances, the purification of the bromine was being
carried out as follows. 1000 grams of chemically pure bromine
were gradually admitted to 700 grams of pure sodium hydrox-
ide contained in sufficient water to dissolve it. In this
manner the bromine was converted into a mixture of bromide and

hypobromite in accordance with the following reaction:-

$$2 \, Na \, OH + Br_2 = Na \, Br + Na \, BrO + H_2O$$

This salt solution was evaporated almost to dryness during which process the hypobromite was converted into bromate as follows:-

$$3 \, Na \, BrO = 2 \, Na \, Br + Na \, Br \, O_3$$

The scum containing the impurities was then poured off with the mother liquor, and the drained crystals placed in a large distilling flask which was fitted to a condensor. From a dropping funnel fitted to the flask, concentrated chemically pure sulphuric acid was added. (All connections were either ground or sealed glass joints). The first and last 10 c.c. of bromine distillate were discarded, and the purified distillate subjected to redistillation in exactly the same manner as before. The bromine was then put aside for use in the run.

(c) Air Calibration of Absorption Bulb.

The absorption bulb (A) was then immersed in sand (contained in a copper beaker) and the temperature of the bath gradually raised until a maximum of 490° was reached. At this temperature the bath was maintained for twelve hours, the bulb all the while being under a partial vacuum of 130 m.m. This was done in order to drive off any moisture which might have entered during the filling and sealing. During the process of heating, one of the stop-cocks was left open to allow the disengaged moisture to escape. The bulb was then evacuated to the lowest pressure obtainable with a mercury pump, and weighed. A series of readings was then taken on the weights of the bulb under different conditions of temperature and pressure in order to determine the amount of air contained in the bulb, and whether or not any of the gases (air) present was absorbed

CURVE No. I.

1 SPACE = 0.0125 GRAMS

← WEIGHT →
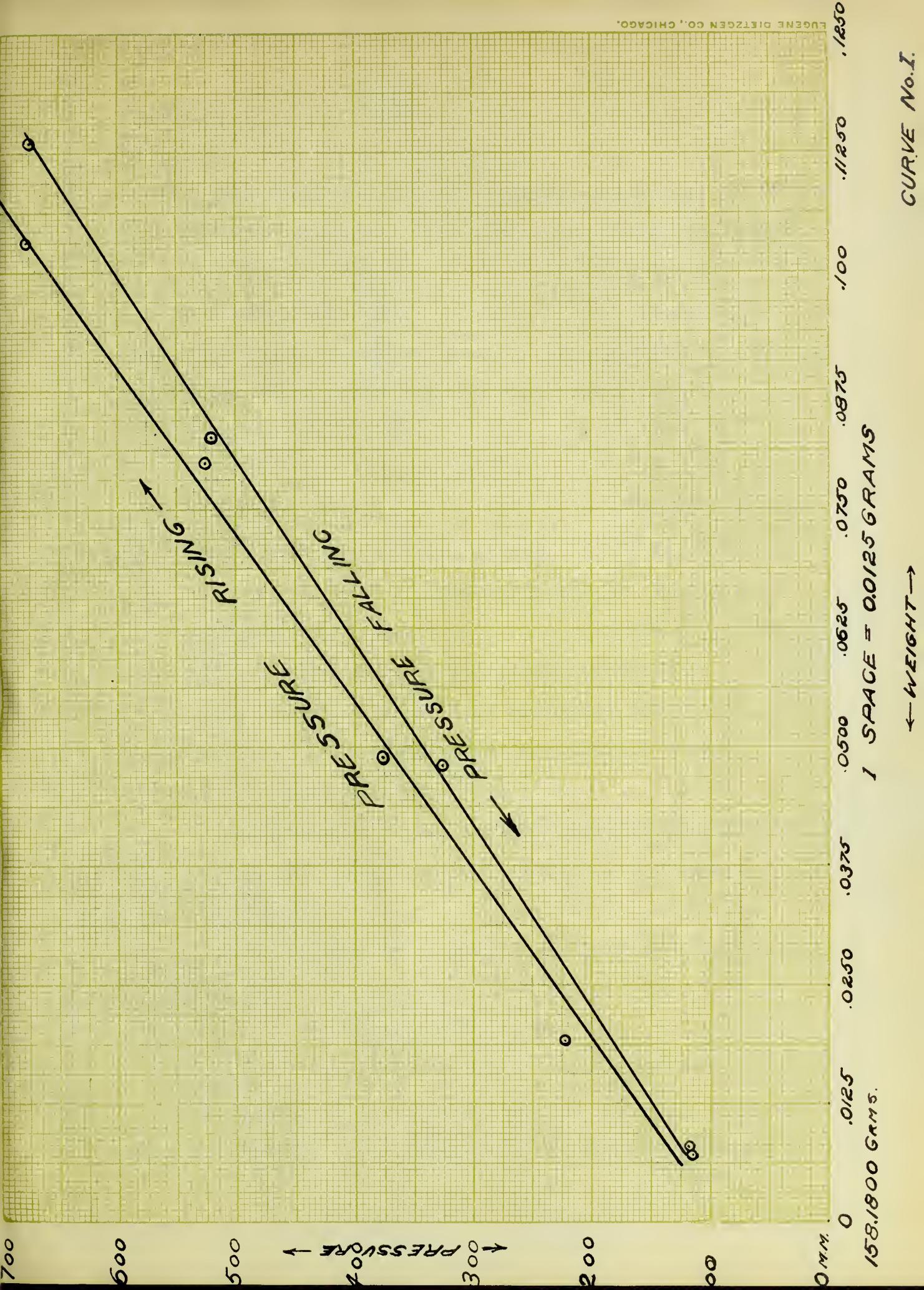
appreciably by the copper sulphate. These values are shown
in plotted form in the curve No.1.

   The data resulting from this determination are as follows :-

      Wt. of bulb empty (dry air)   = 103.4465 grams
      Wt. of bulb + Cu SO_4 = 164.3562 "
      Wt. of Cu SO_4 = 50.9097 "

Some glass wool was then inserted, the neck sealed off, and a
new weight taken under the following conditions :-

      Temperature of bulb   = 27.9 C.
         "   " barometer   = 22.5 C.
      Barometer reading   = 738.90 m.m.
      Correction for air (additive)   =   4.7 m.m.
         "   " 0° (subtractive) = 2.65 m.m.
      Wt. of bulb   = 158.2937 grams
      4.7 − 2.65 = 2.05 m.m. (additive correction)
      738.90 + 2.05 = 740.95 m.m. corrected pressure.
      Difference in pressure in manometer = 0 m.m.
      Final pressure = 740.95 m.m.
      Final pressure corrected to 0° FROM 27.9^o (Bulb temperature) =
      669.3 m.m., and obtained according to following calcu-
      lations,-
      Volume of tube is constant; the pressures vary as the
      absolute temperatures P : Po :: T : To
            740.95 :x :: 301 :273.1
            301x = 740.95 \ 273.1   ∴ x = 669.26

   Data similar to these were taken by changing the pressure
at each reading, first going from atmospheric pressure to zero

millimeters pressure and then back to atmospheric pressure again. The data resulting from these readings which were plotted in curve No. 1, are tabulated as follows :-

No.	Diff.in Press. (Manometer).		Baromet.Press. Reading.	Baromet. Temper.	Corrected Pressure.
1	0.	m.m.	738.90	22.5° C.	740.95
2	174.7	"	739.00	21.0	741.18
3	398.	"	750.10	22.8	752.01
4	569.	"	732.70	21.0	734.90
5	614.	"	740.95	23.37	742.85
6	503.	"	740.50	23.9	748.1
7	333.	"	740.70	24.10	748.3
8	161.5	"	739.65	23.9	741.47
9	0.	"	743.05	25.4	745.65

No.	Final Press.	Press.at Zero.	Temper. of Bulb.	Weight of Bulb.
1	740.95	669.26	27.9° C.	158.2937
2	566.48	515.4	26.5	158.2626
3	354.60	327.6	22.0	158.2380
4	165.9	118.5	25.2	158.1881
5	128.85	117.27	27.0	158.1807
6	245.1	222.95	27.5	158.1991
7	415.3	376.6	28.0	158.2291
8	579.97	527.7	27.5	158.2600
9	745.65	680.7	26.0	158.2832

By taking the difference in pressure and weight in two successive readings, the actual weight and hence the actual vol-

ume of air contained within the flask, can be calculated.

669.26 − 515.4 = 153.86 m.m. difference in pressure

158.2937 − 158.2626 = .0311 grams difference in weight of air.
In as much as the volumes at different pressures are inversely
proportional to their pressures, the mass of a constant vol-
umecan be calculated when two weights are known at two pres-
sures.

Letting V = the original volume of mass M at 0° & 669.3 m.m.,
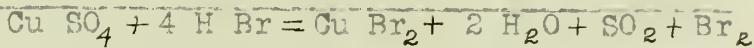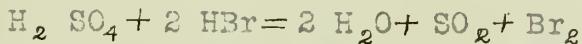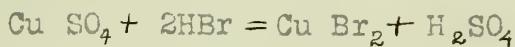
then $\dfrac{158.86 \cdot V}{669.26} = .0311$

$$\therefore V = \frac{.0311 \quad 669.26}{158.86} = .131 \text{ grams of air at } 0^\circ \& 760 = \frac{131}{134} =$$

$$= 970 \text{ c.c.}$$

(d) The Sorption of Hydrogen Bromide.

After a proper adjustment of the apparatus, moisten-red
phosphorus and glass beads were placed in the distilling flask,
and bromine placed in the dropping funnel. The bromine was then
admitted to the distilling flask and allowed to react upon the
phosphorus. The reaction between the latter substance and
bromine gave rise to phosphorus tribromide, which, being in
contact with water, was immediately hydrolysed to hydrogen
bromide and phosphorous acid. The purifying train was then
thoroly flushed out with this gas until it alone was contained
in the train. Then the stop-cock on the absorption bulb(A),
having been previously evacuated to the lowest obtainable
pressure of a mercury pump, was opened slowly, and the hydro-
gen bromide gradually admitted to it. The gas was then per-
mitted to pass thru the apparatus until the copper sulphate

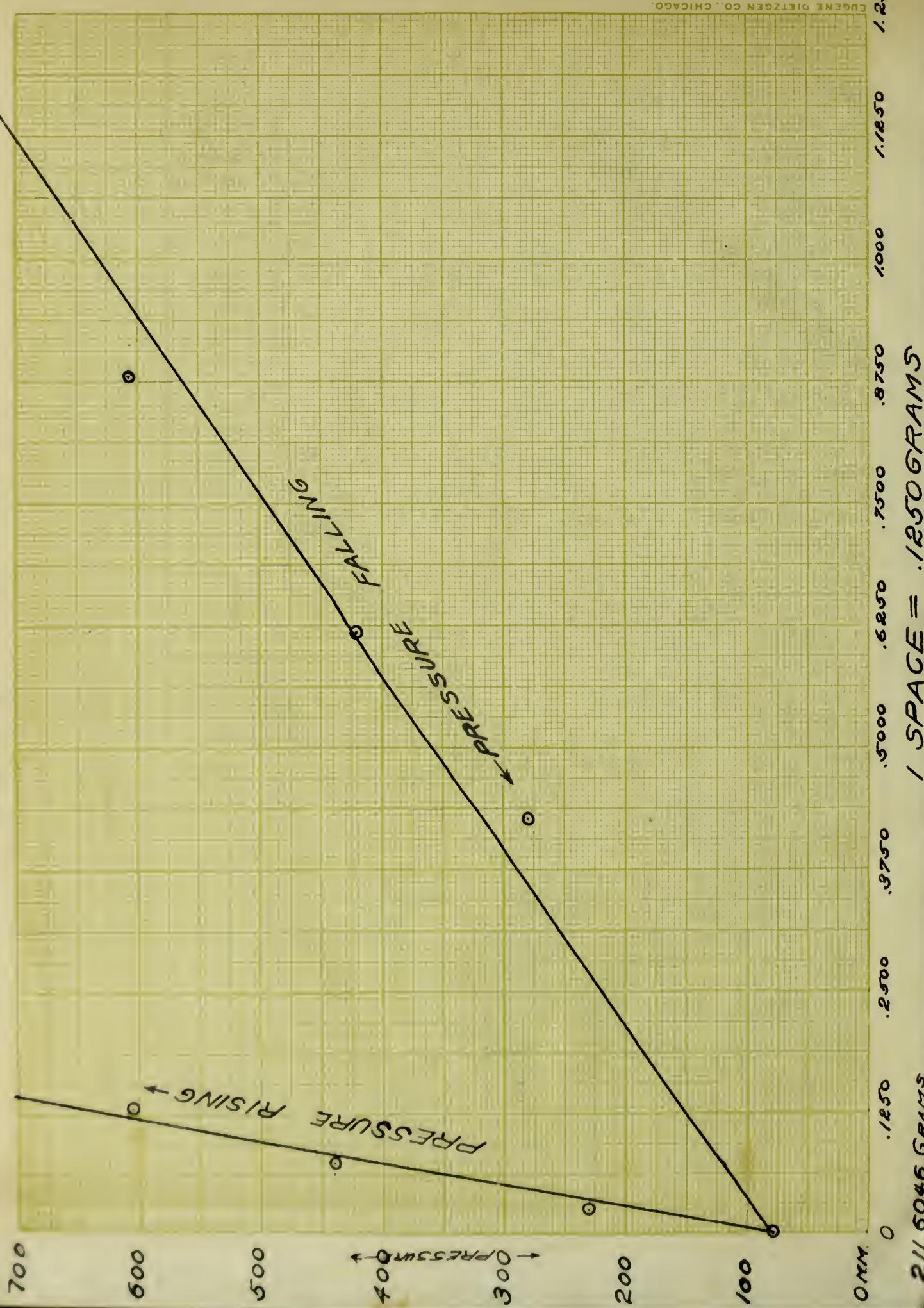had become saturated at atmospheric pressure and zero degrees Centigrade.

Owing to the traces of bromine which appeared to be coming over into the train, it was found necessary to insert two additional , well filled U-tubes containing moistened red-phosphorus and glass beads. In spite of this precaution, however, it was found that bromine was produced in both tubes containing copper sulphate, altho the hydrobromic acid gas entering them was free from bromine. This of course meant that the copper sulphate underwent double decomposition chemical reaction, at least in part, and perhaps entirely, as shown by the following reactions :-

$$Cu\ SO_4 + 2HBr = Cu\ Br_2 + H_2SO_4$$
$$H_2\ SO_4 + 2\ HBr = 2\ H_2O + SO_2 + Br_2$$
$$\overline{Cu\ SO_4 + 4\ H\ Br = Cu\ Br_2 + 2\ H_2O + SO_2 + Br_2}$$

Thus, one of the products of the first double decomposition reaction being a strong oxidizing agent, it reacts with the immediately present hydrogen bromide , a good reducing agent, as seen.

In order to reduce the necessary error (which was smaller the lower the pressure, Br_2 not being absorbed) to a minimum, the reaction was conducted as slowly as possible so as to keep the temperature from rising to any considerable extent. After allowing the reaction ample time for completion, a series of readings was taken, each one being conducted as follows. After sealing the absorption tube to the train, the latter was flushed out several times with hydrogen bromide. Then

HYDROGEN BROMIDE

PRESSURE FALLING

PRESSURE RISING

1 SPACE = .12500 GRAMS

211.6046 GRAMS

EUGENE DIETZGEN CO., CHICAGO.

after the absorption bulb had come to constant temperature
(0 C.), the pump connection was opened and the desired differ-
ence of pressure effected. The inside stop-cock on the bulb
was then opened, and sufficient time allowed for saturation
of the contents at that pressure andtemperature. The pump
connection and the stop-cock regulating the flow of hydrogen
bromide were then turned off, and, after an interval of an
hour , a second reading taken. When the pressure had become
constant, the stop-cock on the bulb (A) was closed, and the lat-
ter detached, thoroly cleaned, and weighed. In this manner a
series of readings was taken from atmospheric down to about 180
m.m.pressure, and then a retrace-series back to atmospheric
pressure.

Altho the weight varied each time in direct proportion to the
pressure, the great divergence in the curve representing the
increasing pressure gave no substantial evidence as to the
nature of the reaction.

(e) Data and Calculations.

The data resulting from this determination are tabulated
below and plotted in curve sheet no. II.

| | | Corrected | | | |
Bar.Pres.	Bar.Temp.	Pressure.	Diff.Pres.	FinalPres.	Wt.of Bulb.
738.5	27.0	740.31	0.m.m.	740.31	212.7841
736.2	24.1	738.01	181. "	719.9	212.4833
734.5	26.4	736.2	312. "	424.2	212.2206
735.30	27.1	736.95	454. "	282.95	212.0338
736.4	30.1	737.6	662. "	75.6	211.8046
734.5	27.0	736.2	495. "	231.2	211.6300
734.7	27.3	736.1	298. "	438.1	211.6796
734.60	27.2	736.05	132. "	604.0	211.7080

735.45   27.1   736.1   O "   736.1   211.7625

Another series of readings was then taken, but it,too, gave an

indefinite result. After several fruitless attempts to obtain

a series of readings which would indicate the nature of the

substance within the bulb, an analysis and several calculations

were made which gave a satisfactory explanation concerning

what went on, what substances were produced, and in what pro-

portions.   The analyses on copper, bromine, and sulphur were

each run in duplicate, and yielded the following results:-

Copper	No.I	21.65	Average	21.73	21.73
"	No.II	21.81			
Bromine	No.I	54.24	"	54.11	54.11
"	No.II	53.98			
Sulphur	No.I	6.47	"	6.42	19.26 SO_4
"	No.II	6.37			
Moisture (By Difference)					4.90
				82.26	100.00

A qualitative analysis of the contents of the wash bottle

(used to collect all gases issuing from the apparatus during

the reaction) showed the presence of hydrobromic acid and sul-

phuric acid, and sulphur dioxide, the sulphuric acid either

having been carried over mechanically or produced from the

oxidation of sulphur dioxide by bromine.

CONCLUSION.

Chapter III.

Conclusion.

(a) Interpretations of Results.

From the nature of the results obtained during the last part of the run, it is very evident that the contents of the absorption bulb can not be considered as a single chemical individual because of its inconstancy in absorbing and giving up gas. This discrepancy, however, is accounted when the nature of the reaction is considered more closely in the light of the analytical results obtained as given above. Thus, an oxidizing agent in the presence of a reducing agent naturally occasions an interaction, which, in the present case,

$$H_2 SO_4 + 2 HBr \rightleftarrows H_2 O + SO_2 + Br_2 \quad .$$

involves five substances, two of which are of such a character as to be retained by the contents of the bulb. The sulphur dioxide and bromine are both volatile under ordinary conditions, but, in this case, the bromine is retained by condensation, and is driven out but slowly by mechanical transfer, while the sulphur dioxide passes off readily. After a considerable amount of gas has been passed, the bromine disappears. Neither of these two substances seems to have any particular affinity for the other substances present. On the other hand the sulphuric acid produced during the first reaction, which escapes subsequent reduction, is practically non volatile at the temperature used, and to a very slight extent . if at all, driven out mechanically.

If water were liberated in the presence of strong sulphuric acid, it is reasonable to suppose that it will be retained for the most part by the latter substance rather than to pass off as a vapor. Hence the substance analyzed contains not only copper bromine and sulphur but undoubtedly considerable water, retained either by the free sulphuric acid, the copper sulphate, or both. Thus the analysis is found to lack 4.90 % of what it should be (when the sulphur has been calculated to $-SO_4-$) if no moisture were present. Reliable check results were obtained on each analysis, and as water is the only substance which could be present under the conditions, it was used to make up the 100 % by difference as shown in sheet no.23.

Now, if moisture and sulphur are neglected and only the copper and bromine considered in a proportion, it is found that the proportion of copper to bromine is almost identical to that of the pure cupric bromide. Thus the total percentage of copper and bromine = 75.84 , the copper factor of which is $\frac{21.73}{75.84} = 28.6$ % , the bromine factor of which is $\frac{54.11}{75.84} = 71.2$ %. The percentage of copper in pure cupric bromide = 28.2 % . The percentage of bromine in pure cupric bromide = 71.7 %. Thus if we subtract the total percentage of copper and bromine from 100 per cent, we have a remainder of 24.16 %, part of which is made up of sulphur. Assuming all sulphur to be present as SO_4 ,and adding the moisture, we have :-

$$\frac{96 \quad 6.42}{32} = 19.26 \text{ % } SO_4$$

$$75.84 \text{ %} + 19.26 \text{ %} + 4.90 \text{ %} = 100 \text{ %}.$$

which is in very close agreement with the results obtained from the run. Thus,

original weight of empty bulb $= 107.3840$

" " " $CuSO_4$ " $= 158.$

" " "$CuSO_4$ ── $= 50.9097$

" " " copper $= \dfrac{63. \quad 50.9097}{160}$

and when calculated to cupric bromide $=$

$\dfrac{\cancel{\emptyset\emptyset} \; '50.9097 \; '223}{160 \quad \cancel{\emptyset\emptyset}} \quad \dfrac{11373}{16} \; = \;$ 69.9 grams of copper bro-

mide.

amount of substance in bulb was found to be :-

$212.7840 - 107.3840 = 105.4001$ grams.

Now from the analysis of this substance the weight should be:-

$.2173 \times 105.4001 = 22.81$ weight of copper.

$.5411 \times 105.4001 = 56.81$ " " bromine.

$.049 \times 105.4001 = 5.145$ " " moisture.

$.1926 \times 105.4001 = \underline{20.2230}$ " " SO_4

Total 104.9000 grams.

In addition to these data which seem to point strongly towards copper bromide as the product of the reaction; other evidence of equal significance and pointing in the same direction was obtained.

Upon dissolving the dry substance in absolute alcohol, it was found that 50 grams of the latter dissolved 10 grams of the substance, leaving no residue, showing the absence of copper sulphate which is insoluble in absolute alcohol. This solution was a dark brown in color, just as is pure cupric bromide

in the same solvent.

To another portion of the substance, water was gradually added, first, with the formation of a dark brown solution (evidently the actual color of cupric bromide molecules) (20) then with the formation of a green transparent solution, and lastly with the formation of a blue solution (due to the actual color of the Cu^+- ions) (20). This is characteristic of cupric bromide in aqueous solution(20).

Still another test of conclusive nature consisted in heating the substance to 300° . During the heating bromine was evolved, leaving a white solid in place of the original black substance. This white residue was entirely insoluble in water. If the original substance had consisted of copper sulphate in which hydrogen bromide was adsorbed, no brominewould have been evolved, but hydrogen bromide instead, and the resulting residue would have been completely soluble in water.

It is not possible to interpret these results as a simple adsorption process since the reaction seems to be a double decomposition in the ordinary sense. On the other hand the pressure diagram does not show any evidence of this reaction since the pressure varies directly as the mass. This may be due in part to the formation of SO_2 during the reaction.

Conclusion.

1. When anhydrous copper sulphate is treated with dry hydrogen bromide at constant temperature and under varying conditions of pressure, a double decomposition chemical reaction ensues in accordance with the following reaction :-

$$Cu\ SO_4 + 2HBr \rightleftharpoons Cu\ Br_2 + H_2\ SO_4$$

going almost completely in the direction indicated by the
upper arrow, with the formation of cupric bromide, sulphuric
acid, and small amounts of other substances as indicated
by the following :-

$$H_2SO_4 + 2\ HBr = SO_2 + 2\ H_2O + Br_2$$

The phenomenon of adsorption seems to have no part whatsoever
in this case.

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